

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

WO 00/69260
PCT/EP00/03946

Colored Compositions Containing Insecticide

The invention relates to polymer-based compositions containing insecticide, said compositions containing at least one dye for the recognition of the point in time at which the insecticide is exhausted, said dye having a different color after the evaporation of the insecticide.

From WO 97/29 634 and 99/01 030 polymer-based compositions containing insecticides are known which give off the active ingredient at high temperature and can be processed into formed bodies (so-called "vaporizer mats"). The insecticides can be vaporized with the aid of heating devices so that the application of the insecticides can be controlled at will.

For vaporizer mats based on cellulose (cardboard) dyes have already been proposed which show the depletion of the active ingredient in the substrate by a change of color. Dyes of this type cannot be used for polymer-based insecticide compositions.

One of the demands which are made on dyes for polymer-based compositions containing insecticide is a homogeneous distributibility in the polymer.

Another demand on such dyes is that no disadvantageous interactions with the insecticide result. One of the preferred insecticides from WO 97/29 634 and 99/01 030 is Transfluthrin, that is, (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid-(2,3,5,6-tetrafluorophenyl)-methylester. The dyes to be used according to the invention should harmonize in particular with Transfluthrin and show its exhaustion by a change of color. Moreover, this change of color should be drastic so that the sudden change in color is easy to recognize.

As active pyrethroid ingredients the following are preferably used:

- 1) 3-allyl-2-methyl-cyclopent-2-en-4-on-1-yl-d/l-cis/trans-chrysanthemate
(Allethrin / Pynamin®),
- 2) 3-allyl-2-methyl-cyclopent-2-en-4-on-1-yl-d-cis/trans-chrysanthemate (Pynamin forte®),
- 3) 3-allyl-2-methyl-cyclopent-2-en-4-on-1-yl-d-trans-chrysanthemate (Bioallethrin®),
- 4) 2,3,5,6-tetrafluorobenzyl-(+)-IR-trans-2,2-dimethyl-3-(2,2-dichlorovinyl)-
cyclopropanecarboxylate (Transfluthrin, Bayothrin®),
- 5) (S)-3-propargyl-2-methyl-cyclopent-2-en-4-on-1-yl-(IR)-cis/trans-chrysanthemate
(Prallethrin / Etoc®),

or mixtures of these active ingredients.

Particularly preferred are the active ingredients 3-allyl-2-methyl-cyclopent-2-en-4-on-1-yl-d-cis-trans-chrysanthemate (Pynamin forte®) and

2,3,5,6-tetrafluorobenzyl-(+)-IR-trans-2,2-dimethyl-3-(2,2-dichlorovinyl)-
cyclopropanecarboxylate (Transfluthrin).

The polymer base underlying the compositions according to the invention contains at least one polymer with a softening range between 100 and 300, preferably between 150 and 250, in particular between 150 and 200°.

The softening range is bounded in the case of amorphous thermoplastic polymers by the vitrification temperature and in the case of partially crystalline polymers by the melting temperature.

As polymeric materials amorphous and partially crystalline polymers as well as mixtures of both are preferably used which can be processed thermoplastically, i. e. as a viscous melt, and whose softening range lies, at normal pressure, below the boiling point of the active ingredients to be incorporated. The polymers for the corresponding active ingredient are chosen so that the active ingredient mixes at least partially with the polymers.

As suitable polymers the following are preferably used.

Soft PVC, polystyrene, styrene/butadiene, styrene/acrylonitrile, acrylonitrile/butadiene/styrene, polymethylacrylate, amorphous polycycloolefins, cellulose esters, aromatic polycarbonates, amorphous aromatic polyamides, polyphenylene ether, poly(ether) sulfones, polyimides, polyethylene, polypropylene, polybutylene, polymethylpentene, hard PVC, polyamide, polyetheramides, polyesteramides, polyoxymethylene, polyethylene terephthalate, polybutylene terephthalate, polyimide, poly(ether)ketone, and polyurethane.

Preferred mixtures are, by way of example,

blends of polycarbonates with polybutylene terephthalate, blends of polyamide-6 and styrene/acrylonitrile, blends of polypropylene and polymethylpentene.

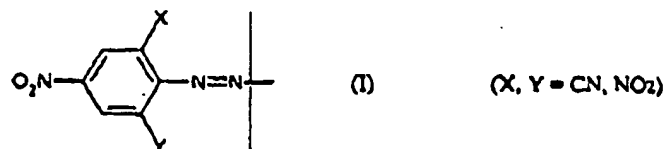
Particularly preferred are polypropylene, poly-4-methyl-1-pentene, and their mixtures.

The compositions according to the invention are preferably based on mixtures containing

A. 0.1 to 80, preferably 0.2 to 40, in particular 0.5 to 20, especially 1 to 12 % by weight

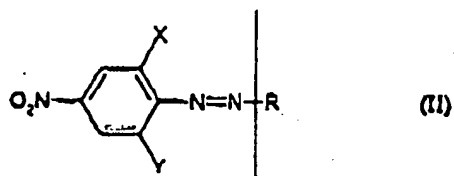
Transfluthrin

Now it has been found that o-cyanazodyes which contain the unit



are exceptionally well-suited for this purpose.

The object of invention are polymer-based insecticide compositions containing dye characterized by the fact that the dye contains at least one compound of the structure

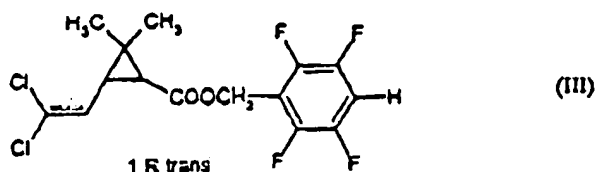


where

X, Y mean, independently of one another, CN or NO₂ (with the understanding it is not permitted that X = Y = NO₂) and

R means an aromatic group, substituted in given cases.

The most important insecticides for the compositions according to the invention are the pyrethroids.



and

- B. 99.9 to 20, preferably 99.8 to 60, in particular 99.5 to 80, especially 99 to 88% by weight poly-4-methyl-1-pentene which for its part can be replaced by another poly- α -olefin up to half, preferably up to one third, in particular up to one fourth of its weight.

where the specified percentages each relate to the total of the components A + B.

Transfluthrin and a process for its production are known from DE-OS 37 05 224 (= EP-PS 279 325).

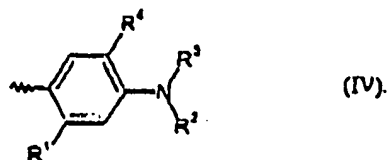
Poly-4-methyl-1-pentene B is a polymerizate, preferably with a vitrification temperature of 50 to 60° C, a softening temperature measured according to Vicat (ASTM D 1525) of 140 to 180° C, preferably 170 to 175°, and a melt index (260° C/5 kg) measured according to ASTM D 1238 from 20 to 200, preferably 22 to 35 [g/10 min] which, as is known, can be produced by polymerization of 4-methyl-1-pentene.

The principal compounds coming into consideration as poly- α -olefins which can partially replace the poly-4-methyl-1-pentene are polyethylenes, polypropylenes, polybutenes, and polyisobutenes as well as copolymerizates of the α -olefins which are the basis of said polymerizates, such as, for example, ethylene/propylene copolymerizates. Preferred polypropylenes include iso- and/or

syndiotactic polypropylenes, preferably with a softening temperature measured according to Vicat (ISO 306) of 130 to 170°, preferably 140 to 160° C, and a melt index (230° C/2 kg) measured according to ISO 1133 for 20 to 40, preferably 25 to 35 [g/10 min].

To the extent that "other" poly- α -olefins are used concomitantly the ratio by weight of poly-4-methyl-1-pentene to poly- α -olefins can be 70:30 to 99:1, preferably 80:20 to 95:5.

For the compound according to structure (II) suitable functional groups R are functional groups of coupling components of the benzo-, naphthalene-, pyridine-, indolo-, and tetrahydroquinoline series, but preferably N-substituted p-aminoaryl groups and in particular anilines of the structure



Therein

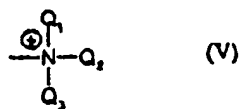
R_1 means hydrogen, C_1 - C_{18} -alkyl, C_1 - C_{18} -alkoxy, C_6 - C_{16} -aryloxy, C_1 - C_{12} -alkylcarbonylamino, C_6 - C_{12} -Ar- C_1 - C_4 -alkylcarbonylamino, C_5 - C_{12} -cycloalkylcarbonylamino, C_6 - C_{15} -arylcarbonylamino, C_1 - C_5 -heterylcarbonylamino, C_1 - C_{12} -alkoxycarbonylamino, C_1 - C_{12} -alkylsulfonylamino, C_6 - C_{15} -arylsulfonylamino, aminocarbonylamino, CN, CF_3 , carbamoyl, di- C_1 - C_6 -alkylaminocarbonyl, C_1 - C_{12} -alkoxycarbonyl, sulfamoyl, di- C_1 - C_6 -alkylaminosulfonyl, or C_1 - C_{12} -alkoxysulfonyl,

R_2 means hydrogen, C_1 - C_{18} -alkyl, C_6 - C_{12} -Ar- C_1 - C_4 -alkyl, or C_6 - C_{15} -aryl,

R_3 means hydrogen, C_1 - C_{18} -alkyl or C_6 - C_{12} -Ar- C_1 - C_4 -alkyl, and

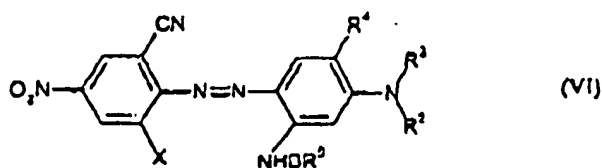
R_4 means hydrogen, C_1 - C_{18} -alkyl, C_1 - C_{18} -alkoxy, C_5 - C_{15} -aryloxy, C_6 - C_{12} -Ar- C_1 - C_4 -alkoxy, halogen, CN, carboxyl, or C_1 - C_{12} -alkoxycarbonyl.

By the alkyl and alkoxy groups (therefore, for example, also alkylsulfonyl or alkoxycarbonyl) mentioned above in arbitrary connection preferably those groups with 1 to 4 atoms are to be understood which preferably are substituted once by OH, CN, halogen, C_1 - C_4 -alkoxy, C_2 - C_5 -alkylcarbonyloxy, or by ammonia groups of the structure



where Q_1 , Q_2 , and Q_3 mean C_1 - C_6 -alkyl, C_5 - C_{12} -cycloalkyl, C_6 -Ar- C_1 - C_4 -alkyl, or C_6 -aryl or alternatively the remaining members of an N-heterocycle such as pyridine, imidazol, and triazol form, while by the aryl or aryloxy groups preferably phenyl or phenoxy groups are to be understood which, in given cases, are substituted once by Cl, Br, NO_2 , CN, C_1 - C_4 -alkoxy, or C_1 - C_4 -alkyl.

Quite particularly preferred dyes correspond to the structure



in which

B means -CO-, -CO₂-, or -SO₂-,

R⁵ means C₁-C₆-alkyl, C₆-Ar-C₁-C₄-alkyl, C₆-aryl, or NV¹V²,

V¹ means hydrogen, C₁-C₁₈-alkyl, C₆-Ar-C₁-C₄-alkyl, or C₆-C₁₂-aryl,

V² means hydrogen, C₁-C₁₈-alkyl or C₆-Ar-C₁-C₄-alkyl,

R² means hydrogen, C₁-C₁₈-alkyl, C₆-Ar-C₁-C₄-alkyl, or C₆-C₁₂-aryl,

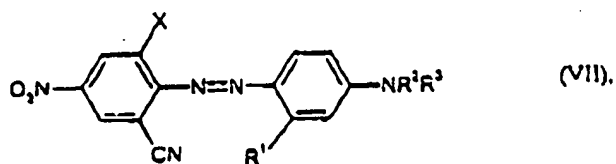
R³ means hydrogen, C₁-C₁₈-alkyl or C₆-Ar-C₁-C₄-alkyl,

R⁴ means hydrogen, C₁-C₁₈-alkyl, C₁-C₁₈-alkoxy, C₆-C₁₂-aryloxy, or C₆-Ar-C₁-C₄-alkoxy

and where preferably the condition should apply that B = -CO- or -SO₂- if R⁵ = NV¹V².

By the alkyl and alkoxy groups preferably those groups with 1 to 4 carbon atoms are also understood here which preferably are substituted once by OH, CN, halogen, C₁-C₄-alkoxy, or C₂-C₅-alkylcarbonyloxy, while by the aryl or aryloxy groups preferably phenyl or phenoxy groups are understood which, in given cases, are substituted once by Cl, Br, NO₂, CN, C₁-C₄-alkoxy, or C₁-C₄-alkyl.

Preferred dyes for the compositions according to the invention correspond to the structure



wherein

X means cyano or nitro,

R² means straight-chained or branched C₁-C₁₀-alkyl, in given cases substituted by halogen, OH, acyloxy, CN, or phenyl, which in turn can be substituted by C₁-C₄-alkyl, or halogen,

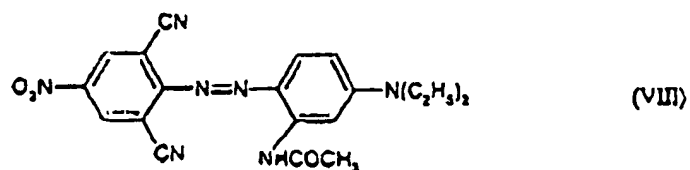
R³ means H and the meanings given for R²,

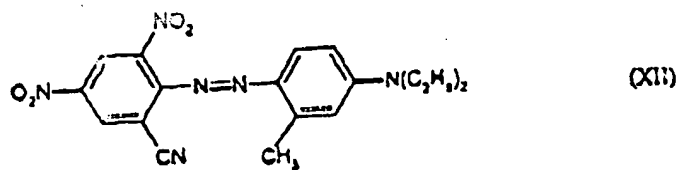
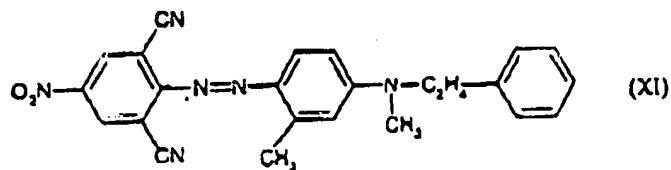
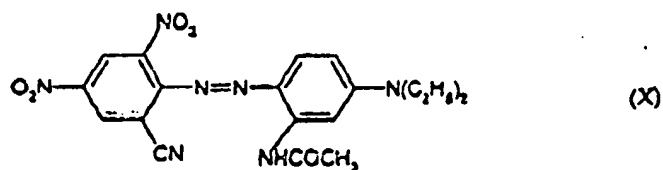
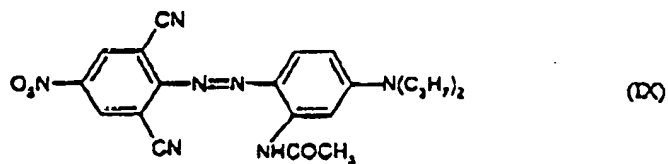
R¹ means H, C₁-C₄-alkyl, C₁-C₈-acylamino, or C₁-C₄-alkylsulfonylamino.

Those dyes of the structure (VII) are preferred wherein

R¹ stands for methyl or acetamino.

Particularly preferred dyes for the compositions according to the invention correspond to the structures





The dyes of the structure (II) and a process for their production are known, cf., for example, DE-OS 24 55 495, to whose disclosed content reference is hereby made.

Most of the dyes used according to the invention color the polymer insecticide compositions reddish blue to blue. A particular advantage of the invention lies in the simple recognizability of the sudden change from colored to colorless.

The compositions according to the invention contain 0.001 to 0.5, preferably 0.006 to 0.15, in particular 0.024 to 0.11 % by weight of dye (II) relative to the total of insecticide and polymer.

The compositions according to the invention contain in general between 0.1 and 80, preferably between 0.2 and 40, particularly preferably between 1.0 and 20% by weight insecticide relative to the total of insecticide and polymer.

As additive substances modification agents and/or fillers and strengtheners and/or processing adjuvants can be used such as, for example, nucleation adjuvants, softeners, release agents, flame-resistance agents, impact-resistance modifiers, stabilizers, or additives otherwise customary in the field of thermoplastics. Preferably fillers are used as are described in the Encyclopedia of Polymer Science and Engineering, Vol. 7, pp. 53 – 73 (1985).

As fillers and strengtheners minerals such as, for example, gypsum, chalk, glass fibers, sand, titanium (IV) oxide, preferably glass fibers, can be used.

The amount of additive substances can fluctuate within wide limits. In general it is 1 to 80, preferably 0.2 to 50, and in particular 0.5 to 30% by weight relative to the additive-containing composition according to the invention.

The compositions according to the invention can be produced by the polymer being introduced as a granulate or powder into a suitable kneader or extruder and plasticized. Under the plastification conditions and temperatures typical for the polymer the insecticide and dye can be introduced and distributed uniformly directly into the polymer melt via a suitable dosing apparatus.

The polymers containing the active ingredient can be granulated in various ways. Either extruded and entirely or partially cooled strands (strand granulation) are cut or the hot melt is cut directly on exit from the nozzle in front of the head (for example, water ring granulation).

The insecticide-containing granulates produced can be processed further thermoplastically into formed parts or be processed with additional polymerizate into mixtures (master batch).

For forming, the processes customarily applied in the case of plastics such as, for example, injection molding, extrusion blowing, foil extrusion, or deep drawing can be used.

The compositions according to the invention can be applied in the form of vaporizer mats in conventional vaporizer devices such as, for example, are used for cellulose vaporizer mats. Operating temperatures of 60 to 180° C, preferably 130 to 170° C, insure a steady, relatively uniform release of active ingredient to the environment.

An additional object of the invention is the use of the compositions according to the invention for combating insects such as, for example, flies and gnats.

The percentages specified in the following examples each relate to weight.

Examples

Example 1 Production of Polymer-Active Ingredient Granulate

1.1 Extrusion Conditions:

Extruder: Brabender PL 2000 Double Screw Extruder
 (35/17D), Screw Type S

Conditions: Temperature 280/280/270/280° C, --100 RPM--
6 kg/h

Screw Filling: ca. 250 g

1.2 Preparations:

- A. Homogenize polymer TPX RT 18 (See Example 3) and dye on an Engelmanns mixer, Type Elite 650 in a 5 L plastic container (3 kg/container).
- B. The BHT (= butylhydroxytoluene) is dissolved in Transfluthrin in the heat (ca. 50°) then filter the solution via glass frit G4.

1.3 Dosing:

TPX RT 18 and dye via a dosing scale of the Engelhardt company, Type 150, and Transfluthrin / BHT with a gear pump of the Ismatec company, Type MV-Z, is dosed into the extruder.

1.4 Granulation:

The strand is drawn off via a water bath (2.5 m long), predried over an interval of water suction, and granulated with a granulator of the Scheer company, Type SGS 50-E. The loss in traverse is ca. 300 g.

Example 2 Injection Molding

Mixing: 100% active ingredient granulate

2.1 Injection Molding Conditions

Equipment: Arburg 320 – 210 – 850, single-shaft screw Ø
35 mm, screw filling ca. 125 g (corresponds to 5
shots)

Temperature Profile: 250° C (nozzle) / 265° C / 270° C / 280° C (reverse
temperature profile)

Cycle Time: 15 sec

Mold Temperature: 30° C

Mold: Cooling channel, 12-part tool, injection via mold
tunnel

Drying Product: ca. 15 h at 50° C in vacuum-drying cabinet

First Running: 10 shots at 25 g

Injection Mold Recycling: 10 – 15% mixing is possible.

Dimensions of the polymer vaporizer mats: 3 mm x 22 mm x 2.5 mm.

Example 3 Formulas for the Polymer Mats with Dyes

The following polymer vaporizer mats were produced according to the process stated above.

Example	Composition	Amount (%)
3.1	TPX*	91.261
	Transfluthrin (washed Al ₂ O ₃)	8.300
	BHT**	0.415
	Dye XII	0.024
3.2	TPX*	91.261
	Transfluthrin (washed Al ₂ O ₃)	8.300
	BHT**	0.415
	Dye XII	0.024
3.3	TPX*	91.255
	Transfluthrin (washed Al ₂ O ₃)	8.300
	BHT**	0.415
	Dye XII	0.030
3.4	TPX	91.040
	Transfluthrin	8.300
	BHT	0.415
	Titanium Dioxide (@Bayer Titanium R-FK-2)	0.200
	Dye XII	0.040
3.5	TPX	91.245
	Transfluthrin	8.300
	BHT	0.415
	Dye XII	0.040

* TPX = poly-4-methyl-pentene of the Mitsui company (polymethylpentene TPX RT 18)

** BHT = butylhydroxytoluene

Example 4 Test of the Sudden Change in Color

The following methodology describes the test of the endpoint display (sudden change in color) of polymer vaporizer mats by visual evaluation of the change in color of the mats.

At least 3 test mats are used per trial. The test mats are pushed into the heating devices provided so that they lie in the center of the heating block of each device. Thereafter the heating devices with the test mats are plugged into the switched-off male connector.

The switching clocks are set to the test period defined.

Of the possible test period models

- | | | |
|----|---------------------------|----------|
| a. | 8 h damping period / day | 1 cycle |
| b. | 24 h damping period / day | 3 cycles |

model a was preferably used.

After the expiration of the damping period defined for each, all the mats are removed from the heating devices and tested with an untreated reference sample with regard to a change in color.

The endpoint recognition is insured if the indication of color of the test product used can be clearly distinguished visually from that of the unused product, for example:

- sudden change from dark blue to amber
- clear fading of the color of the test product.

Evaluation of the Vaporizer Mats from Example 3

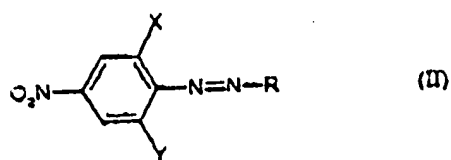
Example	Formula No.	Evaluation
4.1	3.1	++
4.2	3.2	++
4.3	3.3	+
4.5	3.5	++

+ Discoloration clearly visible

++ Discoloration very clearly visible

Claims:

1. Polymer-based compositions containing insecticide and dye characterized by the fact the dye contains at least one compound of the structure

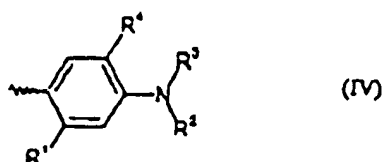


where

X, Y mean, independently of one another, CN or NO₂ (with the understanding it is not permitted that X = Y = NO₂) and

R means an aromatic group, substituted in given cases.

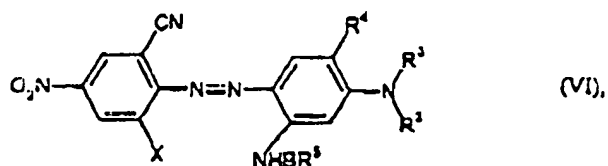
2. Compositions according to claim 1 wherein R in the structure (II) stands for



where

- R_1 means hydrogen, C_1 - C_{18} -alkyl, C_1 - C_{18} -alkoxy, C_6 - C_{16} -aryloxy, C_1 - C_{12} -alkylcarbonylamino, C_6 - C_{12} -Ar- C_1 - C_4 -alkylcarbonylamino, C_5 - C_{12} -cycloalkylcarbonylamino, C_6 - C_{15} -arylcarbonylamino, C_1 - C_5 -heterylcarbonylamino, C_1 - C_{12} -alkoxycarbonylamino, C_1 - C_{12} -alkylsulfonylamino, C_6 - C_{15} -arylsulfonylamino, aminocarbonylamino, CN, CF_3 , carbamoyl, di- C_1 - C_6 -alkylaminocarbonyl, C_1 - C_{12} -alkoxycarbonyl, sulfamoyl, di- C_1 - C_6 -alkylaminosulfonyl, or C_1 - C_{12} -alkoxysulfonyl,
- R_2 means hydrogen, C_1 - C_{18} -alkyl, C_6 - C_{12} -Ar- C_1 - C_4 -alkyl, or C_6 - C_{15} -aryl,
- R_3 means hydrogen, C_1 - C_{18} -alkyl or C_6 - C_{12} -Ar- C_1 - C_4 -alkyl, and
- R_4 means hydrogen, C_1 - C_{18} -alkyl, C_1 - C_{18} -alkoxy, C_5 - C_{15} -aryloxy, C_6 - C_{12} -Ar- C_1 - C_4 -alkoxy, halogen, CN, carboxyl, or C_1 - C_{12} -alkoxycarbonyl.

3. Compositions according to claim 1 wherein the dye contains at least one compound of the structure



wherein

D means -CO-, -CO₂-, or -SO₂-,

R⁵ means C₁-C₆-alkyl, C₆-Ar-C₁-C₄-alkyl, C₆-aryl, or NV¹V²,

V¹ means hydrogen, C₁-C₁₈-alkyl, C₆-Ar-C₁-C₄-alkyl, or C₆-C₁₂-aryl,

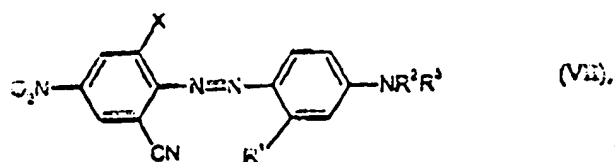
V² means hydrogen, C₁-C₁₈-alkyl or C₆-Ar-C₁-C₄-alkyl,

R² means hydrogen, C₁-C₁₈-alkyl, C₆-Ar-C₁-C₄-alkyl, or C₆-C₁₂-aryl,

R³ means hydrogen, C₁-C₁₈-alkyl or C₆-Ar-C₁-C₄-alkyl,

R⁴ means hydrogen, C₁-C₁₈-alkyl, C₁-C₁₈-alkoxy, C₆-C₁₂-aryloxy, or C₆-Ar-C₁-C₄-alkoxy and where preferably the condition should apply that B = -CO- or -SO₂- if R⁵ = NV¹V².

4. Compositions according to claim 1 wherein the dye contains at least one compound of the structure



wherein

X means cyano or nitro,

R² means straight-chained or branched C₁-C₁₀-alkyl, in given cases substituted by halogen, OH, acyloxy, CN, or phenyl, which in turn can be substituted by C₁-C₄-alkyl, or halogen,

R³ means H and the meanings given for R²,

R¹ means H, C₁-C₄-alkyl, C₁-C₈-acylamino, or C₁-C₄-alkylsulfonylamino.

5. Compositions according to claim 4 wherein

R² stands for straight-chained C₁-C₄-alkyl or phenylpropyl,

R³ stands for straight-chained C₁-C₄-alkyl, and

R¹ stands for methyl or C₁-C₄-acylamino.

6. Compositions according to claim 1 wherein the insecticide is Transfluthrin.
7. Compositions according to claim 1 wherein the polymer is polymethylpentene.
8. Compositions according to claim 1 which contain 0.001 to 0.5% by weight dye of the structure (II), 0.1 to 80% by weight insecticide, and 1 to 80% by weight polymer, each relative to the total of insecticide and polymer.
9. Use of the compositions according to one of the preceding claims for combating insects.